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Vapor pressures and isopiestic molalities of concentrated $CaCl_2$(aq), $CaBr_2$(aq), and NaCl(aq) to $T = 523$ K ☆

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Abstract

The Oak Ridge National Laboratory high-temperature isopiestic apparatus was outfitted with precise pressure gauges to allow for direct vapor pressure measurements. Vapor pressures over concentrated solutions of $CaCl_2$(aq), and $CaBr_2$(aq) were measured at temperatures between (380.15 and 523.15) K in the range of water activities between 0.2 and 0.85. Isopiestic molalities were used to determine osmotic coefficients at the conditions where NaCl reference standard solutions remained undersaturated. The main goal of this work was to improve the accuracy of isopiestic comparisons based on the calcium chloride reference standard. Osmotic coefficients for $CaCl_2$(aq) and $CaBr_2$(aq) calculated from both isopiestic and direct vapor pressure results were combined with the literature data and used to build general thermodynamic models based on a variant of extended Pitzer ion-interaction equations and valid at the saturation pressure of water. While these empirical models approach the accuracy of the experimental data in a wider range of concentrations and temperatures than any previously published equations, considerable amounts of accurate data and a substantial effort are required in order to obtain a satisfactory representation using power series-based virial equations. The effect of experimental uncertainties on the accuracy of the direct vapor pressure results is discussed, including in particular the error caused by the presence in the apparatus of a small amount of CO_2. The substantial decrease of the solubility product of $CaCO_3$ in concentrated chloride solutions at temperatures above 423 K is a serious defect of calcium chloride as a water activity reference standard.
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1. Introduction

Aqueous $CaCl_2$ is the most common 2-1 electrolyte found in a wide range of concentrations in natural terrestrial and marine environments, in industry, agriculture and biology. While calcium chloride has been often considered a troublesome waste produced in large quantities by the Solvay soda-ash process, its uses tended to increase, and today it is even deliberately produced through the reaction of limestone with HCl or by refining of natural brine. Besides the most common high-volume uses for road deicing and dust control, $CaCl_2$ is used as a drying agent for gases and liquids, ammonia or carbon dioxide absorbent, as "high-density brines", often in combination with $CaBr_2$ and other salts, in drilling and maintaining gas and oil wells, as a cement accelerator, as a working fluid in energy conversion systems including heating and refrigeration units using solar energy, in food processing, and in other applications.

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Thermodynamic properties of aqueous calcium chloride are quite accurately known at $T = 298.15$ K and at elevated temperatures and moderate molalities up to about 5 $\text{mol} \cdot \text{kg}^{-1}$, but uncertainties increase rapidly with increasing temperature for both very dilute and very concentrated solutions. Due in part to its much wider concentration range, $CaCl_2$(aq) is not characterized nearly as well as NaCl(aq), the representative 1-1 electrolyte. While high solubility in water, along with low price and low toxicity make calcium halides attractive in many applications, even less data exist for the more soluble $CaBr_2$. An accurate and comprehensive representation of its excess properties could justify a more widespread use of $CaCl_2$(aq) as a convenient primary isopiestic reference standard covering the range of water activities extending from saturation to below 0.2, at temperatures where sulfuric acid becomes too corrosive and even volatile. The most common isopiestic standard, NaCl(aq), reaches the state of saturation as water activity drops below about 0.75.

From the theoretical point of view it is desirable to compare and explain the behavior of various ionic solutes in wide ranges of temperature and composition. The existing interpretations have been usually limited to more or less arbitrary assignments of varying degrees of importance to a collection of several mechanisms, which often have opposite effects on macroscopic properties. These mechanisms have included creation of multiple solvation shells, electrostatic (Bjerrum) ion pairing, solvent-induced ion pairing, solvent-separated ion pairing (local hydrolysis), hydrogen-bonded-structure breaking and structure making, negative hydration, and hydrophobic hydration. Although abundant fragmentary descriptions of ion–solvent interactions have been published in the literature to rationalize various segments of the experimental database, there is no general picture of the behavior of even the simplest aqueous electrolytes, consistent enough to accommodate all the results available for anions and cations of varying sizes, and provide any predictive capabilities. The changes of solution properties with the sizes of the ions turn out to be complex and difficult to predict. For example, in the sequence $MgCl_2(aq) \leftarrow CaCl_2(aq) \rightarrow CaBr_2(aq)$, where, starting from $CaCl_2$, the calcium is replaced by magnesium or the chloride is replaced by bromide, the result is in both cases a decrease in vapor pressure, or an increase in the activity of the ions, for reasons that are not well understood on the molecular scale. This is reflected in the continuing difficulties in explaining the behavior of the activity coefficients of alkali metal and alkaline earth metal halides in aqueous solutions, even qualitatively [1].

Global thermodynamic models, even though they are largely empirical, provide convenient representations of thermodynamic properties for practical applications and for further research. The Pitzer ion-interaction formalism [2,3], where the short-range interactions between species are represented by virial coefficients, has been widely used since its introduction to implement such models. One of the advantages of using essentially the same model for all solutes and their mixtures is the opportunity to compare the properties and find even subtle differences in their properties. The behavior of concentrated $CaCl_2$(aq), the premier example of a 2-1 electrolyte, was found to be "anomalous" at $T = 298.15$ K by Phutela and Pitzer [4], since it deviates from the simpler pattern of $MgCl_2$(aq) starting at about 4.5 $\text{mol} \cdot \text{kg}^{-1}$. While sixth and even seventh-order interaction terms (corresponding to the fifth and sixth powers of the molality) were used in equations fitting accurately the behavior of concentrated $CaCl_2$(aq) [4,5], the usual Pitzer treatment through the third order is sufficient for a satisfactory representation of the behavior of $MgCl_2$ solutions to saturation.

Parameters of Pitzer equations, valid to moderate concentrations, are available for a large number of electrolytes at $T = 298.15$ K. However, relatively few general models of any kind have been reported that extend to elevated temperatures and concentrated solutions. Although the temperature dependence of the parameters in such general models is entirely empirical, they are widely used as convenient and relatively compact representations of large sets of experimental data of varying accuracy and relevance. Among the three 2-1 type salts mentioned above, general thermodynamic models which are based on extensive collections of various experimental results and valid in a wide range of temperatures and concentrations exist for $MgCl_2$(aq) and $CaCl_2$ but not for $CaBr_2$. The general thermodynamic model for $MgCl_2$(aq) developed by Wang *et al.* [6] is based on experimental results at molalities extending to 25 $\text{mol} \cdot \text{kg}^{-1}$, temperatures to 627 K and pressures to 100 MPa. Precise isopiestic measurements and equations for this system, valid to 4 $\text{mol} \cdot \text{kg}^{-1}$, were previously reported by Holmes *et al.* [7,8].

Phutela and Pitzer [4] obtained a general thermodynamic model for $CaCl_2$(aq), by fitting ion-interaction equations to ambient temperature enthalpy and vapor pressure results, and using the earlier isopiestic results of Holmes *et al.* [7] extending to 473 K to correlate the second and third virial coefficients with temperature. Ananthaswamy and Atkinson [5] described another model valid to higher molalities (9 $\text{mol} \cdot \text{kg}^{-1}$) but only to $T = 373$ K. This model is based on a variant of the ion-interaction equations extending through the sixth virial coefficient [9]. The third representation of the osmotic and activity coefficients of $CaCl_2$(aq) was published in the form of CODATA series tables [10], where the recommended values are given at molalities to 11 $\text{mol} \cdot \text{kg}^{-1}$ and $T = 373.15$ K. Finally, the only pressure-dependent general equations for $CaCl_2$(aq) were developed by Holmes *et al.* [11,12]. This accurate